Evolution of GaSb epitaxy on GaAs(001)-$c(4\times4)$

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The growth of GaSb films by molecular beam epitaxy on GaAs(001)-$c(4\times4)$ at 490 °C has been studied *in situ* with scanning tunneling microscopy and *ex situ* with transmission electron microscopy. As the film is deposited, four distinct growth regimes are observed: the first two monolayers grow layer by layer with platelet-like two-dimensional (2D) islands; the next monolayer forms coherently strained three-dimensional (3D) quantum dots; further deposition induces film relaxation and rough 3D growth; for film thicknesses >100 nm the growth is again 2D, proceeding via spiral growth around emerging threading dislocations. The atomic-scale mechanisms inherent in the transitions between the growth regimes are discussed. Variations in growth procedures aimed at improving the quantum dot uniformity and reducing the dislocation density are proposed.

I. INTRODUCTION

The epitaxial growth of GaSb on GaAs(001) is of technological interest for a number of reasons. A few monolayers of GaSb deposited under appropriate conditions grow into uniformly sized, three-dimensional (3D) islands known as quantum dots.[1–3] These coherently strained dots, as well as other similar III–V semiconductor dots, have novel optical properties and may lead to the development of planar electro-optical devices.[3–5] Thicker epilayers of GaSb on GaAs(001) are often used as a template for the growth of InAs/GaInSb and InAs/AlSb heterostructures that are promising candidates for use in long-wavelength optical and high-speed electronic devices.[6] Due to the lattice mismatch between GaSb and GaAs (+7%), however, epilayers a few microns thick typically have a high density of threading dislocations.[7] Because such dislocations may negatively impact device performance, considerable effort has been applied to their characterization in III–V semiconductor films, with the goal of developing growth procedures that minimize their density.[8–12]

The evolution of GaSb films on GaAs(001) is known to involve a variety of growth modes as a function of thickness, as shown by reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), and transmission electron microscopy (TEM).[1–3,12] The first two to three monolayers (ML) grow layer by layer, with further deposition leading to 3D growth initiated by the formation of coherently strained quantum dots.[1–3] It has been proposed that the formation of such dots, in general, is intrinsically related to the structure of the initial two-dimensional (2D) wetting layer,[13] though this layer has yet to be observed for GaSb on GaAs. For 3D films >10 ML, TEM (Refs. 7, 9, and 10) and x-ray scattering experiments[8] reveal very regular arrays of 90° misfit dislocations at the GaSb–GaAs interface. As 3D growth progresses, these misfit dislocations merge and yield threading dislocations that propagate away from the interface. When the film thickness reaches 1 μm, 2D layer-by-layer growth is again observed, and is dominated by spiral growth around the threading dislocations.[12] To date, very little work has explored the transitions between the different growth regimes; specifically, the mechanism for the initial nucleation of the dots, the transition from dots to dislocated films, and the transition to spiral growth. In this article we describe the surface morphology and film structure of GaSb overlayers from a single monolayer to several microns thick grown by molecular beam epitaxy (MBE) on GaAs(001), as observed *in situ* with scanning tunneling microscopy (STM) and *ex situ* with TEM. In addition to describing the rich gallery of structures present on these overlayers, we propose atomic-scale mechanisms for the evolution of the growing GaSb epilayers.

II. EXPERIMENT

Experiments were carried out in an interconnected, multichamber ultrahigh vacuum (UHV) facility that includes a III–V semiconductor MBE chamber and a surface analysis chamber with STM. Si-doped GaAs(001) substrates (17×17 mm), oriented to within 0.1° of (001), were mounted on a custom-designed sample holder that mounts onto both a standard 5-cm-diam MBE sample block and the stage of a custom-modified commercial STM.[14] After thermally removing the oxide, a 1-μm-thick buffer layer of GaAs (Si doped at 10^{16} cm^{-3}) was grown at 580 °C at a growth rate of 1 ML (0.28 nm)/s (as determined by RHEED oscillations). An additional 30 nm of undoped GaAs was then grown at a lower growth rate (0.1 ML/s) with frequent growth interrupts, eliminating Si contamination on the growth front and producing large, atomically ordered terraces. Following GaAs buffer layer growth, the substrate was cooled to 490 °C under an As_4 flux, stabilizing the $c(4\times4)$ reconstruction. Undoped GaSb was then grown at 0.1 ML/s (1 ML GaSb=0.30 nm).[2] For thick films, the growth rate was increased to 1.0 ML/s after depositing the first 33 ML at the slower rate. After the GaSb film growth was completed, the sample was held at 490 °C under an Sb_4 flux for 140 s, cooled to room temperature under no flux, and then transferred to the STM. All STM

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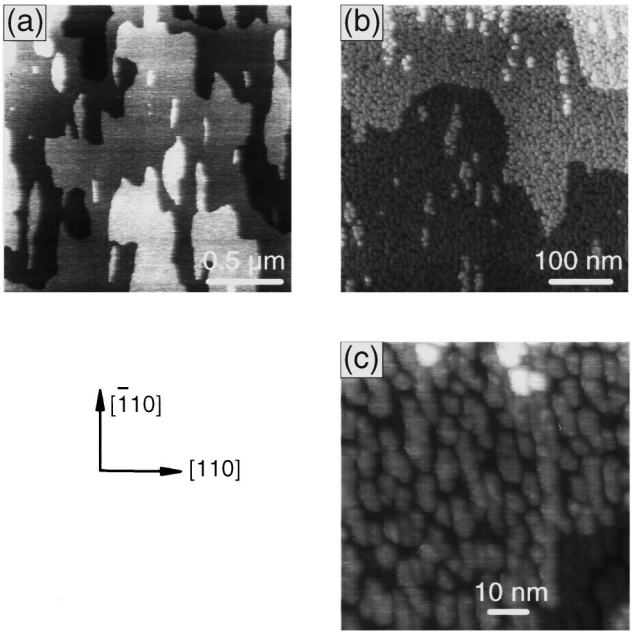

FIG. 1. Filled-state, gray-scale STM images of (a) a clean GaAs(001)-$c(4\times4)$ substrate, (b) a surface after deposition of 1 ML of GaSb, and (c) 1 ML GaSb at higher magnification showing the discontinuous 2D structure of the wetting layer. Each change in gray level represents a single monolayer height step (~0.3 nm).

images displayed were acquired in constant-current mode with currents between 0.1 and 0.5 nA and sample biases ranging from -0.3 to -3.0 V.

III. RESULTS

The GaAs buffer layer surface consists of large, atomically smooth terraces (~0.5 μm wide) with few islands or pits separated by monolayer-height (0.3 nm) steps, as shown in Fig. 1(a). Atomic-resolution images (not shown) reveal a well ordered, low defect density $c(4\times4)$-reconstructed surface, consistent with RHEED. After deposition of 1 ML of GaSb, the underlying GaAs terrace structure can still be observed [Fig. 1(b)], including large terraces (>0.5 μm wide) and a few large islands (>50 nm wide). The smaller islands (<50 nm wide) are attributed to second layer GaSb growth. Significant differences between the clean GaAs(001)-$c(4\times4)$ substrate and the GaSb-covered surface are apparent when the surface is viewed at higher magnification [Fig. 1(c)]. A network of interconnected 2D island-like structures (''platelets'') ~10 nm in diameter are observed, with narrow $\leqslant1$ ML deep gaps between them. The gaps, or vacancy arrays, within this wetting layer tend to order into meandering lines. When a second monolayer of GaSb is added, it grows predominantly on top of the first layer platelets, maintaining the platelet diameter but increasing the thickness to 2 ML.

Upon addition of a third monolayer of GaSb on GaAs(001) the growth becomes 3D [Stranski–Krastanov (SK) growth], as indicated in Fig. 2(a). The 3D hillocks (the quantum dots discussed earlier) are 9 ± 1 nm (32 ± 3 ML) high and of uniform size, with a number density of ~100 μm^{-2}, consistent with previous *ex situ* AFM measurements.[2,3] Because the shape and diameter of high aspect ratio structures such as these dots are difficult to determine accurately with scanning probe microscopy (due to tip shape convolution effects), we have also examined the dots by TEM. In plan-view TEM images of a sample with 2.5 ML of GaSb, the dots appear to be elliptical, with a major diameter of ~15 nm, and are free of dislocations.[3] Significantly, STM images of the surface between the dots reveal that a wetting layer is still present, indicating that the dots are not formed via 3D coarsening of the wetting layer. This indication is also supported by an analysis of the total amount of GaSb contained in the dots observed at 3 ML total coverage: the volume of each dot, $\sim\pi$ (7.5 nm)$^2\times$32 ML, is sufficient to cover a (75 nm)^2 area with a ML thick film of GaSb. At the observed number density, ~1/(100 nm)^2, this corresponds to ~0.6 ML of surface coverage contained within the dots; i.e., the initial 2-ML-thick wetting layer is intact.

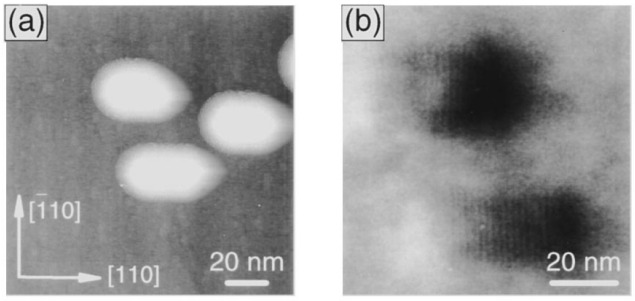

FIG. 2. (a) STM image of 3 ML of GaSb showing three 9-nm-high quantum dots. Note that the apparent dot shape and lateral dimensions include substantial tip-convolution effects. (b) TEM image of 5 ML of GaSb showing two larger 3D islands that have relaxed (as indicated by the moiré fringes observed).

After a total of 5 ML of GaSb has been deposited, TEM reveals that the dots have grown in size and that their density is reduced to ~50 μm^{-2}, indicating some of the dots have merged. Within the dots moiré fringes are observed [Fig. 2(b)], implying the dots have relaxed to the larger GaSb lattice constant and misfit dislocations have formed. The 3D growth and coalescence of the dots continues as the film grows, greatly roughening the surface, as illustrated by the STM image of a 10-nm (33-ML)-thick epilayer shown in Fig. 3(a). The surface of this film is very rough with no resolvable terrace-like features. Although a large density of threading dislocations are certainly present in this film,[9] their emergence at the surface cannot be observed in the STM image given the degree of surface roughness.

For a film thickness of 100 nm, the transition back to 2D layer-by-layer growth has occurred [Figs. 3(b) and 3(c)]. At this thickness the surface of the GaSb has well-defined terrace edges and is becoming ordered on the atomic scale. A large density of threading dislocations are seen emerging from the surface, ~50 μm^{-2}, including many dislocation half-loops. As the film thickness increases, the dislocations tend to annihilate one another, such that, when the film thick-

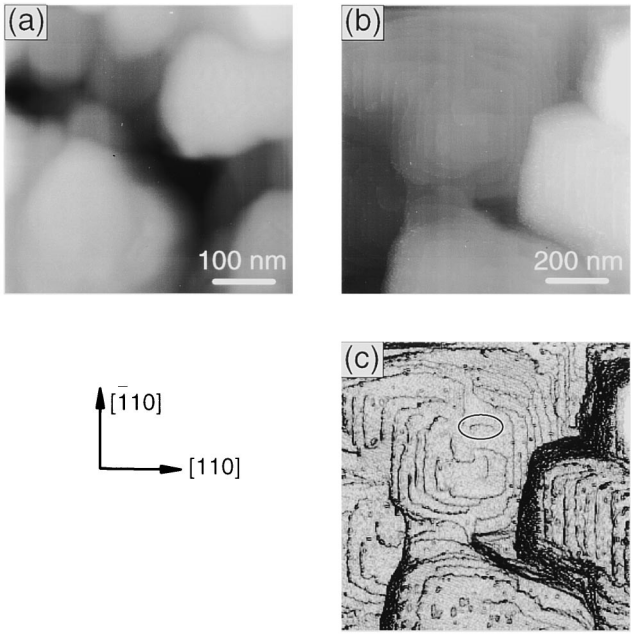

FIG. 3. STM images of (a) 10-nm-thick GaSb film (gray-scale range ≈50 nm), (b) 100-nm-thick film (range ≈10 nm). (c) Image from (b) processed to highlight the terraces and step edges; one of the many dislocation half-loops at the surface is circled.

ness reaches 1 μm, their density is reduced by an order of magnitude to $\sim 5\ \mu m^{-2}$ [Fig. 4(a) and 4(b)]. At this point the film grows in a spiral mode, producing pyramidal structures with one or more threading dislocations emerging at the top and ~50-nm-wide terraces winding down towards the bottom. By varying the temperature used at the end of the growth the surface of the spirals can be terminated with a variety of reconstructions.[15] An atomic-resolution image of an Sb-rich $(2\times5)/c(2\times10)$-reconstructed surface is displayed in Fig. 4(c) illustrating the high degree of atomic-scale order attainable on the surface. A model for this structure will be presented elsewhere.[15]

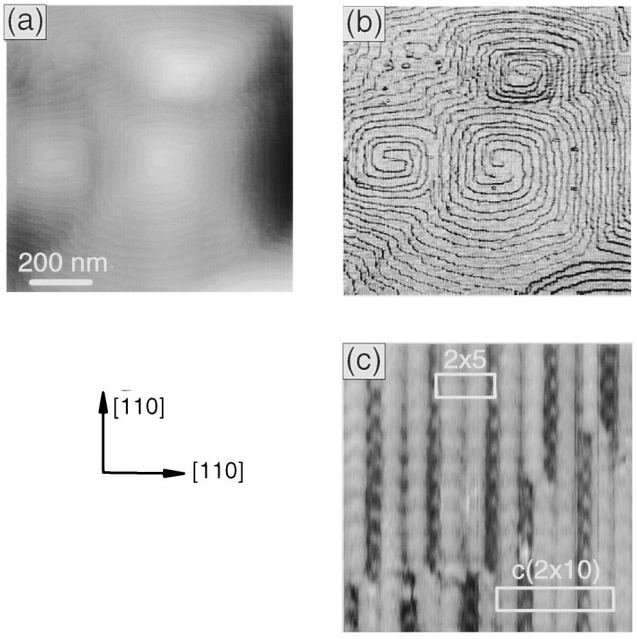

FIG. 4. (a) STM image of 1-μm-thick GaSb film (gray-scale range ≈6 nm). (b) Image from (a) processed to highlight the terraces and step edges. The spiral growth is clearly evident, with threading dislocations visible at the top of the spirals. (c) Atomic-resolution filled-state image (0.3 V, 0.1 nA) on a spiral terrace showing the GaSb(001)-$2\times5/c(2\times10)$ reconstruction. The 2×5 unit cell is 0.86×2.16 nm.

IV. DISCUSSION

We have directly observed that the first two monolayers of GaSb grow on GaAs(001)-$c(4\times4)$ as a discontinuous 2D film. The structure of this wetting layer can be attributed to the effects of the compressive strain: GaSb island growth is limited by the strain buildup, leading to the formation of uniformly sized islands separated by narrow, stress-relieving vacancy lines. Although to our knowledge this is the first observation of such an effect for strained III–V semiconductor monolayers, similar vacancy ordering has been observed for compressively strained epitaxial Ge monolayers on Si(001).[16]

During the deposition of the third monolayer of GaSb on GaAs(001), the growth changes from 2D to 3D as quantum dots appear. Recently, Priester and Lannoo have proposed that the narrow size distribution of such quantum dots is directly related to the presence of a specific type of wetting layer.[13] In their theoretical model, based on a strained heteroepitaxial system where dots form at 1.4 ML, the first monolayer forms a continuous 2D film, whereas the next 0.4 ML grows as a random spatial distribution of large, single-sized ML-height islands. They predict that the second-layer islands become unstable upon further growth, causing each second-layer 2D island to condense into a smaller diameter, 3D dot composed only of the atoms originally in the island. This model does not appear to be the mechanism we observe: the GaSb dots on GaAs(001)-$c(4\times4)$ grow on top of a relatively unaltered 2-ML-thick discontinuous wetting layer and large, single-sized islands are not observed.

Once the formation of dots has occurred, it is generally observed that the next monolayer deposited is incorporated primarily into new dots, and only secondarily onto existing dots (increasing their size).[2] For GaSb on GaAs this behavior changes at some point between 3 and 5 ML, because by 5 ML the dots have grown greatly in size, decreased in number, and relaxed via formation of dislocations. Prior to dislocation formation, the stress within each dot produces a strain field in the surrounding substrate.[17] We propose that as the number density of dots increases and their strain fields increasingly overlap, the net strain in some dots exceeds the threshold required for dislocation formation. Once a dot relaxes, it then becomes a low-energy site for future growth, both from further deposition and from the decay of nearby strained dots (i.e., Ostwald ripening).[18] The preferential growth of these relaxed 3D structures leads to rapid, uneven film growth and adjacent dot coalescence. As the film thickness increases, the relaxed regions continue to grow rapidly

and coalesce, producing the very rough surface observed at 10 nm thickness [Fig. 3(a)].

The transition from 3D back to 2D growth has occurred by 100 nm thickness. At this point the film is completely relaxed and the (001) surface should again be the lowest energy surface for growth. Hence, additional growth tends to eliminate step bunches, promoting (001) terrace formation and smoothing the growth front. As the film further flattens with increasing thickness, spiral growth around the emergent threading dislocations begins.

Our observation of the GaSb wetting layer on GaAs(001)-$c(4\times4)$ points to possible improvements in the growth procedure used to produce quantum dots. If the dot size distribution depends on the platelet size distribution in the initial wetting layer, a better-ordered vacancy array (i.e., more uniform platelet size) should result in more uniformly sized dots. Perhaps growing the wetting layer at a higher temperature or annealing the surface after the growth will have such an effect. Alternately, the GaAs substrate surface can be prepared with a different surface reconstruction having a different unit cell size and symmetry; changing the surface reconstruction may change the wetting layer structure, providing another means to vary the size and shape of the quantum dots.

The procedure used to grow the first few monolayers of GaSb on GaAs may ultimately determine the structure of much thicker films (e.g., buffer layers). As shown by Kang *et al.*,[9] dislocations in relaxed 3D islands nucleate as arrays of 90° misfit dislocations near the GaSb/GaAs interface. These misfit arrays are related to the fact that every 13 unit cells of GaSb are coincident with 14 unit cells of GaAs, so that there is an extra half-plane of GaAs atoms every 56 Å in both of the $\langle 110\rangle$ directions. When two dislocated structures coalesce with the arrays of extra half-planes randomly aligned, threading dislocations may form at their intersection.[9] Hence, the larger the 3D structures are when they merge, the fewer threading dislocations there should be in the resulting continuous film (i.e., if the growth of a low density of large dots can be promoted, the final dislocation density should decrease). Recalling that once a quantum dot relaxes it becomes the lowest energy site for further growth,[18] growing at a reduced rate and higher temperature should promote growth on relaxed regions by inhibiting the nucleation of new dots and enhancing the adatom diffusion rate. This prediction is supported by the observations that with increasing growth temperature the size of 3D InAs islands on GaAs increases,[5] and the density of threading dislocations in thick AlSb films on GaAs decreases.[19]

The growth procedure proposed for lowering the threading dislocation density will necessarily yield a rougher growth surface because it enhances growth of the largest 3D structures. As a consequence, a thicker film will be required to transition back to 2D layer-by-layer growth. If a thin, smooth film is desired rather than a film with a minimum of dislocations, the growth temperature should be decreased. The lower growth temperature will inhibit diffusion, resulting in GaSb growth that is more uniformly distributed across the surface (versus concentrated on a few large 3D islands). Therefore, when the film is fully relaxed (at ~10 nm), the surface should be smoother than it would be following higher temperature growth (albeit with a larger density of threading dislocations). At this point, growth at the higher temperature could be resumed to promote a rapid transition ($\ll 1$ μm) to 2D spiral growth.

V. CONCLUSIONS

We have used *in situ* STM and *ex situ* TEM to study the evolution of GaSb films grown by MBE on GaAs(001)-$c(4\times4)$ at 490 °C. We observe four growth regimes as a function of coverage. The first 2 ML of GaSb forms a discontinuous 2D wetting layer consisting of platelet-like islands separated by vacancy arrays. The third monolayer forms regularly sized, coherent 3D quantum dots on top of the wetting layer. At ~5 ML the interface strain begins to induce relaxation of the dots via dislocation formation, leading to enhanced 3D growth on the relaxed structures and concomitant roughening of the film surface. Full relaxation of the film precedes the transition back to 2D growth at ~100 nm, where a large density of threading dislocations is observed. As the film thickens further, the dislocation density drops due to mutual annihilation, with the film eventually growing in atomically ordered spirals ($\geqslant 1$ μm thickness). Based on the apparent mechanisms responsible for the different growth regimes, prudent variation of the growth procedures should make it possible to improve the quantum dot uniformity, and either reduce the dislocation density or, alternately, reduce the overlayer film thickness required to achieve spiral growth.

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[1] F. Hatami *et al.*, Appl. Phys. Lett. **67**, 656 (1995).
[2] B. R. Bennett, R. Magno, and B. V. Shanabrook, Appl. Phys. Lett. **68**, 505 (1996).
[3] B. R. Bennett, P. M. Thibado, M. E. Twigg, E. R. Glaser, R. Magno, B. V. Shanabrook, and L. J. Whitman, J. Vac. Sci. Technol. B (to be published).
[4] P. M. Petroff and S. P. DenBaars, Superlat. Microstruc. **15**, 15 (1994).
[5] A. Madhukar, Q. Xie, P. Chen, and A. Konkar, Appl. Phys. Lett. **64**, 2727 (1994).
[6] A. G. Milnes and A. Y. Polyakov, Solid-State Electron. **36**, 803 (1993).
[7] R. N. Kyutt, R. Scholz, S. S. Ruvimov, T. S. Argunova, A. A. Budza, S. V. Ivanov, P. S. Kop'ev, L. M. Sorokin, and M. P. Sheheglov, Phys. Solid State **35**, 372 (1993).
[8] A. Bourret and P. H. Fuoss, Appl. Phys. Lett. **61**, 1034 (1992).

[9]J. M. Kang, M. Nouaoura, L. Lassabatère, and A. Rocher, J. Cryst. Growth **143**, 115 (1994).
[10]J. M. Kang, S.-K. Min, and A. Rocher, Appl. Phys. Lett. **65**, 2954 (1994).
[11]C. C. Hsu, J. B. Xu, I. H. Wilson, T. G. Andersson, and J. V. Thordson, Appl. Phys. Lett. **65**, 1552 (1994).
[12]B. Brar and D. Leonard, Appl. Phys. Lett. **66**, 463 (1995).
[13]C. Priester and M. Lannoo, Phys. Rev. Lett. **75**, 93 (1995).
[14]L. J. Whitman, P. M. Thibado, F. Linker, and J. Patrin, J. Vac. Sci. Technol. B **14**, 1870 (1996).
[15]P. M. Thibado, B. R. Bennett, B. V. Shanabrook, and L. J. Whitman (unpublished).
[16]J. Knall and J. B. Pethica, Surf. Sci. **265**, 156 (1992).
[17]See, for example J. Y. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy* (Academic, Boston, 1993).
[18]J. Drucker, Phys. Rev. B **48**, 18 203 (1993).
[19]P. M. Thibado, B. R. Bennett, R. J. Wagner, B. V. Shanabrook, and L. J. Whitman (unpublished).